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Nitrate isotopes in catchment hydrology: Insights, ideas and implications for models

Ioannis Matiatos [a,*], Christian Moeck [b], Yuliya Vystavna [c], Hannu Marttila [d], Natalie Orlowski [e,f], Søren Jessen [g], Jaivime Evaristo [h], Mathieu Sebilo [i], Gerbrand Koren [h], Elias Dimitriou [a], Sasha Müller [g], Yiannis Panagopoulos [j], Michael P. Stockinger [k]

[a] Hellenic Centre for Marine Research, Institute of Marine Biological Resources and Inland Waters, Greece
[b] Eawag - Swiss Federal Institute of Aquatic Science and Technology, Switzerland
[c] International Atomic Energy Agency, Isotope Hydrology Section, Austria
[d] Water, Energy and Environmental Engineering Research Unit, University of Oulu, Finland
[e] University of Freiburg, Hydrology, Freiburg im Breisgau, Germany
[f] Institute of Soil Science and Site Ecology, TU Dresden, Dresden, Germany
[g] Section of Geology, Department of Geosciences and Natural Resource Management, University of Copenhagen, Denmark
[h] Copernicus Institute of Sustainable Development, Utrecht University, Utrecht, Netherlands
[i] Sorbonne Université, CNRS, INRAE, IRD, UPD, UPEC, Institute of Ecology and Environmental Sciences – Paris, iEES, 75005 Paris, France
[j] Department of Hydraulics, Soil Science and Agricultural Engineering, Aristotle University of Thessaloniki, Greece
[k] University of Natural Resources and Life Sciences, Vienna, Department of Water, Atmosphere and Environment, Institute of Soil Physics and Rural Water Management, Muthgasse 18, 1190 Vienna, Austria

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ABSTRACT

Models that simulate water flow and quality, particularly related to nitrate ions, are commonly used on a catchment-scale. However, tracking nitrate ions is a challenging task due to the intricate processes that affect them, such as phase exchanges, transformations, and interactions with various environmental media. In general, models capable of carrying out all tasks required to simulate water flow and quality at the same time, are rare. Additionally, most available models focus only on specific compartments of the watershed, such as surface water, topsoil, unsaturated zone, or groundwater. Taken together, these two challenges can lead to oversimplified representations of a system's hydrology, as catchment internal processes become neglected due to missing information (lack of informative measurements, or models not focusing on all watershed compartments). Attempting to combine these models or to couple different watershed compartments results in complex calculations, increased run times, and a large number of parameters to estimate. Artificial Intelligence (AI) models have been massively used in environmental studies but, so far, the majority of them have been tested theoretically and not under real conditions. To overcome these challenges, stable isotope data are often employed to calibrate and validate internal catchment processes of these models. While water stable isotopes ($\delta^{18}O$ and $\delta^{2}H$ of H_2O) have been extensively used in many water flow models, the use of nitrate isotopes ($\delta^{15}N$ and $\delta^{18}O$ of NO_3^-) in water quality models remains poorly explored. Nitrate isotopes can help trace the origin of NO_3^- contamination and disentangle the complex reactions and dynamics that nitrate undergoes during transport. Hence, we propose that incorporating nitrate isotopes into catchment-scale water flow and quality models can substantially enhance the accuracy of these models. This review provides an overview of the current use of catchment hydrological models in predicting flow and fate of solutes. We discuss their limitations and highlight the potential of combining these models with nitrate isotopes. Ultimately, this approach may reduce prediction uncertainties and provide more effective guidance for water management decisions.

* Corresponding author.
E-mail address: i.matiatos@hcmr.gr (I. Matiatos).

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1. Introduction

The SDG6 (Sustainable Development Goal 6) "Clean Water and Sanitation" is a global goal adopted by the United Nations General Assembly in 2015. It aims to ensure access to clean water and sanitation for all people, as well as improving water quality and increasing water-use efficiency. However, the global nitrogen (N) delivery to surface waters has increased from 44 to 71 Tg N/yr during the period 1970–2015, which is the result of a global increase in anthropogenic source contribution from 60 to 74 % (Beusen and Bouwman, 2022). Furthermore, ~20 % of global studied aquifers were found to be highly contaminated on nitrate (NO_3^-), making nitrates as one the most widely spread contaminant among N-species (Abascal et al., 2022).

Nitrate (NO_3^-) pollution in aquatic systems is a major environmental problem primarily as a result of anthropogenic activities, such as agricultural activities through the use of N-containing fertilizers, sewage disposal, and animal breeding operations (Fig. 1). Nitrate is known for its detrimental effects on surface water ecosystems, particularly causing eutrophication and hypertrophication in rivers, lakes and coastal areas (Townsend-Small et al., 2007; Romanelli et al., 2020). These conditions often lead to algae blooms, fish kills, and other ecosystem-scale changes (Kharbush et al., 2023). On the other hand, exceedance of threshold levels of nitrate in drinking water can lead to a condition called methemoglobinemia, or "blue baby syndrome," which can be fatal for infants (Fan and Steinberg, 1996). Nitrate is also a precursor in the formation of N-nitroso compounds (NOC), which are carcinogens and teratogens, and may result in cancer, birth defects, or other adverse health effects (Schullehner et al., 2018; Ward et al., 2018; Picetti et al., 2022). Overall, nitrate pollution in aquatic systems is a problem of global concern that requires effective strategies to control.

Increased N availability enhances terrestrial productivity; however, excessive soil N input often leads to nitrate leaching into ground- and surface waters. For example, nitrate leaching can originate from forestry activities (harvest, litter, etc.), and especially drainage operations for organic soils in Nordic conditions (Marttila et al., 2018). However, nitrogenous species undergo changes in various environments, such as in soils and the subsurface (saturated and unsaturated zone), surface water, in the hyporheic zone, at the suspended particles of the overlying water above the sediment, and in riparian zones. These nitrogen transformations are heavily influenced by the presence of oxygen and can vary depending on the location. For example, in oxic conditions, organic tissue is broken down and released as ammonium (NH_4^+), which can then be transformed into nitrite (NO_2^-) and nitrate (NO_3^-) through a process called nitrification (Taillardat et al., 2019). However, in anoxic conditions, nitrate can be reduced to non-reactive N_2 through denitrification (Li et al., 2019a). Denitrification is mediated by heterotrophic bacteria and occurs mostly at higher than the topsoil depths and at the water–sediment interfaces. In topsoils where oxygen levels vary, both nitrification and denitrification can potentially take place at the same time (Hall et al., 2016). Additionally, nitrate can also undergo other transformations, such as dissimilatory anaerobic reduction to ammonium (DNRA), while ammonium in the presence of nitrite may undergo anaerobic oxidation to N_2 through the anammox process (Zhou et al., 2014). These transformations are controlled by a combination of factors, such as the presence of electron donors, e.g., organic carbon (Trudell et al., 1986; Steiness et al., 2021), sulfides (Postma et al., 1991; Böhlke et al., 2007), and ferrous iron (Postma, 1990; Korom et al., 2012), the presence of a microbial community to transform nitrogen (Juncher Jørgensen et al., 2009; Torrentó et al., 2010), and the residence time of water (Petersen et al., 2020a,b; Steiness et al., 2021), which links it to catchment water flow.

Nitrate concentration levels in water bodies can be the result of N sources and biogeochemical transformations. For instance, lysimeters experiments in soils showed that the nitrate that leaches under the subroot zone is not directly the combination of the sources of nitrogen but mostly reflects a "new" nitrate produced from the mineralization/nitrification of the soil organic matter (Sebilo et al., 2013). Furthermore, N accumulation in the root zones and the soils, particularly in long-term fertilized areas, creates a time lag in the response of any land-use changes and the N concentrations in the water bodies. Moreover, the inherent delay of N transport through the unsaturated and saturated zone creates another time lag (Baillieux et al., 2015). The delay in the transport of water and nutrients in surface waters and groundwater through soil and the unsaturated zone depends on their hydraulic properties and heterogeneity (e.g., hydraulic conductivity, porosity, thickness of the unsaturated zone), known as hydraulic legacy, and the occurrence of biogeochemical processes (e.g., rates of organic N mineralization), known as biogeochemical legacy (Van Meter et al.,

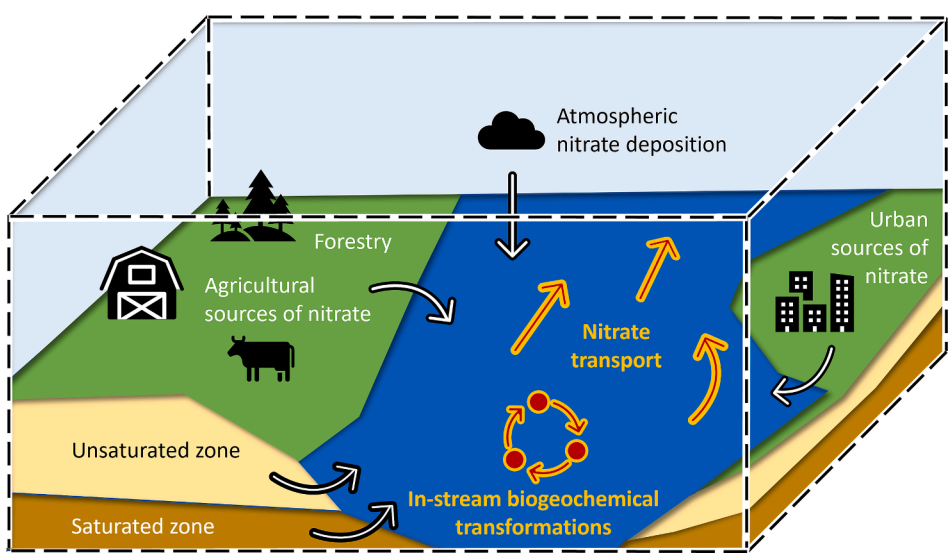

Fig. 1. Conceptual overview of nitrate dynamics in a water catchment with potentially large spatial and temporal variations. The white arrows indicate different pathways for pollution to enter into surface waters, including emissions (1) from beneath the surface; (2) from forested areas, agricultural and urban sources; and (3) through atmospheric deposition (note that this is an illustrative selection, not an exhaustive list of possible nitrate sources). Further in-stream biogeochemical transformations (e.g., nitrification) and variations in the water flow itself (red arrows) affect the nitrate levels along the stream. Nitrate isotopes ($\delta^{15}N$, $\delta^{17}O$, $\delta^{18}O$) are sensitive to the different pollution sources and cycling histories and can, possibly combined with water isotopes, provide additional constraints for models. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2016; Vero et al., 2018).

The efficient monitoring and forecasting of the amount, flow, and quality of water, particularly regarding nitrate pollution levels, is necessary for sustainable water resources management (Burri et al., 2019). Using models to simulate water quantity (including flow) and quality (including solute and reactive transport) in a river catchment under different scenarios can help to anticipate the effects of different water and nutrient management strategies and provide stakeholders with information on how to protect the water resources and remedy the negative impact on them (e.g., Gong et al., 2019; Peña-Arancibia et al., 2019; Zhang et al., 2020a; Hrachowitz et al., 2021; Son et al., 2022). The different scenarios of interest are diverse, such as changing climatic conditions (Fu et al., 2019), land use management and change (Lei et al., 2022) or the impact of dams (Zhang et al., 2011). In a broad sense, a distinction can be made between water quality and water quantity (or synonymous used water flow) models to describe two different environmental processes. Water quantity (or flow) models describe water flow through, for example, the integrated land surface, surface water and groundwater, whereas water quality models attempt to simulate changes in pollutant concentrations as they move through the environment, including water quantity. This can be done on a smaller scale or, as we consider, mostly on a catchment scale and therefore represent catchment models. We use the term catchment models to encompass models that simulate and predict water quality and quantity (including flow) in streams or rivers, groundwater and soil at a catchment-scale. Modeling the flow of water through a catchment and the transport and reaction of solutes regarding water quality is becoming an increasingly interdisciplinary field. Due to this complexity, there are various models and concepts for simulating processes within a catchment, which are overall divided into physically-based models and conceptual models. The definition and examples of these different model concepts are provided in section 3.

To make well-informed decisions, it is important to use models that are validated against real-world measurements of fluxes (e.g., runoff, and nutrient/pollutant loads) and state variables (such as soil water content and groundwater levels). In recent years, modern sensors have led to obtaining high frequency solute data (Bogena et al., 2018; Mennekes et al., 2021). This has increased data availability and amount for model evaluation, allowing models to have a high spatiotemporal resolution when estimating catchment water flow and solute transport. Despite the wide variety of methods for measuring fluxes and state variables as well as modern sensors, catchment heterogeneity can never be investigated in all its detail and thus, uncertainty in the obtained results remains (Moeck et al., 2020). Furthermore, many catchments do not have spatiotemporal high-resolution data and suffer from a lack of data that is especially an issue when trying to predict water flow or solute transport in regions where monitoring is difficult or not possible (Razavi and Coulibaly, 2013; Ramón et al., 2021). In addition to data-related challenges with model validation, it is important to choose the 'right model', as different models are suited for different processes and locations, especially when simplified models are used (e.g., Baginska et al., 2003; García et al., 2016; Smith et al., 2016; Akanegbu et al., 2018).

Different types of transport and reaction models can be used to study water quality dynamics at different scales and levels of complexity. For example, geochemical models, which are typically used to analyse the chemical reactions in natural or engineered geological systems quantitatively based on a set of mathematical equations, help to predict at how water, soil, and rock interact to determine the main reactions and changes that affect water quality on commonly small-scale model applications. In contrast, catchment models often use descriptions of chemical and biological processes to predict water quality at the catchment or hydrological response unit (HRU) level (Neitsch et al., 2011; Nguyen et al., 2019). Similarly, models that focus on simulating water flow throughout a catchment vary in complexity from simple models that fit a sine wave to tracer data (such as $\delta^{18}O$ and $\delta^{2}H$ of H_2O) to obtain fast runoff components (Jasechko et al., 2016; Kirchner, 2016) to complex, soil water flow models (Fang et al., 2015; Saari et al., 2020), and integrated models that fully couple surface and groundwater components (Brunner and Simmons, 2012; Ala-Aho et al., 2015; Moeck et al., 2015; Schilling et al., 2019). Both water flow and quality models operate at different temporal and spatial scales. Hydrological water flow studies for example focus on short-term flow dynamics (e.g., peak flows), short- and long-term water age dynamics (Stockinger et al., 2014; Birkel et al., 2020), and the long-term impact of different land uses on flow dynamics (e.g., Orlowski et al., 2016; Zaherpour et al., 2018). Similarly, water quality models can be used to predict water chemistry over a range of timescales and from various sources, depending on the solute of interest. For example, nitrate studies often focus on longer timescales (Frind et al., 1990; Zhang et al., 2013; Jessen et al., 2017; Matiatos et al., 2019), while studies of phosphorous or pesticide dynamics tend to focus on short-term storm dynamics (Paudel et al., 2010; Rosenbom et al., 2014; Rosenbom et al., 2015; Dupas et al., 2018; Gassmann, 2021; Dagès et al., 2023).

There is a wide range of catchment-scale models for both water quality and flow modeling. This is partly because of new scientific discoveries that have led to improved or completely new models, and partly because of the specific environmental conditions at the sites where the models have been developed. Different physiographical and climatic conditions require different descriptions of processes for various hydrological compartments, especially for simplified models, which increases the computational power required. A common approach is to simplify less important, secondary processes, which has led to a relative disconnection between the catchment hydrological (water flow) and water quality (solute transport) scientific communities and their respective models (Hrachowitz et al., 2016). Models that focus on solute transport tend to rely on simplified representations of hydrological processes through water flow routines, while water flow models are not designed for routing solutes through a catchment or modeling their biogeochemical dynamics. While many water flow models at the catchment scale use water stable isotopes ($\delta^{18}O$, $\delta^{2}H$) as tracers to explicitly account for both effects of pressure propagation and actual water flow (Beven and Germann, 2013), they do not account for the transport or concentration changes of nutrients or contaminants due to biogeochemical reactions (O'Donnell and Hotchkiss, 2019). Water stable isotopes are regularly used as tracers in water flow models because they provide additional information regarding actual water transport. For example, they can help differentiate between water from precipitation, snowmelt, and groundwater discharge, and quantify the relative contributions of each source to a stream or aquifer, and also give estimation of the water age in the catchment. In this regard, they are valuable tools for refining these models by ruling out unrealistic solutions (e.g., Stadnyk et al., 2013; Tetzlaff et al., 2018; He et al., 2019).

On the other hand, AI models (i.e., Machine Learning (ML) and Deep Learning (DL)), have been increasingly used in river water quality and other environmental-related (e.g., climatology, agriculture) studies (Tiyasha et al., 2021). AI models are inspired by the learning mechanisms of the human brain and were initially introduced in the 1950′s (McCarthy, 1956). Machine Learning (ML) techniques are reliable tools in delivering exceptional predictive accuracy, making them particularly valuable for applications involving uncertain processes (Zhang et al., 2020b). These applications are often called "black-box" predictions, offering accurate results but lacking in providing a mechanistic understanding of the systems under study (e.g., Kim et al., 2021; Muñoz-Carpena et al, 2023). Beyond their predictive accuracy compared to mechanistic models (Adnan et al., 2021) ML techniques can help unveil the fundamental principles governing hydrological systems (e.g., Chang and Zhang, 2019; Bortnik and Camporeale, 2021; Nearing et al., 2021), identifying key factors within datasets (e.g., Vystavna et al., 2021), imputation of missing data (e.g., Sahoo and Ghose, 2022), emulating computationally intensive models (e.g., Lim and Wang, 2022), or enhancing the resolution of remote sensing products (e.g.,

Srivastava et al., 2013).

Modeling the transport of nitrate (NO_3^-) is a complex task due to the various reactions and dynamics that need to be taken into account. Nitrogen transport models, similar to those for other contaminants, are typically based on a hydrological model, since water serves as the transport medium for NO_3^-. However, the non-conservative nature of nitrate and its biogeochemical transformations present challenges for these models. Disregarding changes to nitrate concentrations due to biogeochemical reactions, most of the observed spatiotemporal variability of nitrate is an effect of hydrological variability. In this regard, the movement of nitrate is governed by hydrological transport principally through advection, dispersion and less through molecular diffusion.

Nitrate isotopes constitute a powerful tool to trace the origin of nitrate pollution in aquatic systems given that conventional chemical indicators are incapable of unravelling what NO_3^- concentrations in rivers or aquifers embody at any point in time, apart from regulatory pollutant exceedances (Xue et al., 2009; Nestler et al., 2011; Fenech et al., 2012; Blarasin et al., 2021). This is because different natural and anthropogenic sources of nitrate pollution, such as agricultural runoff, sewage wastes, and atmospheric deposition, have relatively distinct isotopic signatures (section 2) and are closely linked to land use practises. For example, Voss et al. (2006) found an increasing contribution from manure and septic wastes in water quality degradation as the percent of agricultural and urban land in the rivers of the Baltic Sea catchment increased. In another study, Yue et al. (2017) used nitrate isotopes to show that the Yellow River catchment undergoes nitrate pollution from variable sources; soil N in the upper section and chemical fertilizer and manure wastes in the lower section, particularly in the low flow season. Using nitrate isotopes, Li et al. (2019b) showed that fertilizer application accounted for 43 % of the total anthropogenic solute inputs to the Wei River, the largest tributary of the Yellow River. More recently, nitrate isotope techniques showed that organic wastes from point and non-point sources are the dominant source of nitrate pollution in many European rivers (Matiatos et al., 2023).

Nitrate isotopes provide insights into complex nitrogen-related processes (e.g., nitrification, denitrification), which help disentangle the system's resilience to pollution and the fate of nitrogen contaminants in the catchment. For example, Suárez et al. (2019) applied nitrate isotope techniques in an agricultural catchment and revealed that soil microbial nitrification was the most important contributor to the nitrate in the river runoff compared to direct leaching of nitrate from mineral fertilizers and atmospheric nitrate deposition. Wang et al. (2021a) found that biogeochemical processes, such as nitrification and sedimentary denitrification, co-existed in different parts of the Jiulong River Estuary, with variable dominance of the first over the latter depending on the hydrological conditions. In a global survey, Matiatos et al. (2021) showed that N-cycling processes are temperature and climate dependent and that sources of nitrate pollution are more probable to be detected during winter.

Despite being a powerful tool in hydrological studies, nitrate isotopes have never been used as part of catchment hydrology models. Similar to water stable isotopes being used in water flow models to improve the representation of catchment-internal processes, we argue that nitrate stable isotopes can be useful tools in improving the transport and biogeochemical reaction routines of water quality models. In this regard, here we provide a general overview of nitrate isotope characteristics and reactions, and various catchment water flow and quality models and AI models, before discussing the limitations of these models and what would be needed for nitrate stable isotopes to be incorporated into models to improve results. We do this by synthesising both recent papers that reflect the current development in the field, and some older key papers that have had a major impact and are still relevant to date. In doing so, we highlight both modelling and observational methods, and also reflect on potential ways forward for this field. In the following sections, the principles, and uses of nitrate isotopes (section 2) and catchment-scale water quality models (section 3) will be discussed, as well as limitations of these models and how nitrate isotopes could help overcome them (sections 4, 5).

2. Nitrate isotopes

NO_3^- is composed of nitrogen (N) and oxygen (O). Nitrogen has two stable isotopes, ^{14}N and ^{15}N, which have a relative abundance of 99.63 % and 0.37 %, respectively (Rosman and Taylor, 1998). Oxygen has three stable isotopes, ^{16}O, ^{17}O, and ^{18}O, with a relative abundance of 99.76 %, 0.037 %, and 0.20 %, respectively. The "δ" (delta) notation, which expresses the relative difference of the ratio of the rare-to-common stable isotope to an international standard, is given in per mil (‰). Thus, the delta value of isotopes is given by:

$$\delta_{sample}(‰) = \left(\frac{R_{sample} - R_{std}}{R_{std}}\right) \times 1000‰ \quad (1)$$

where R is the absolute ratio of $^{15}N/^{14}N$ for nitrogen and $^{18}O/^{16}O$ or $^{17}O/^{16}O$ for oxygen of the sample R_{sample} and the reference material R_{std}, respectively. The international standard for N is atmospheric nitrogen (Mariotti, 1983), for which the ratio $^{15}N/^{14}N$ is 0.003673, whereas for oxygen isotopes it is VSMOW with values $^{18}O/^{16}O = 2005.2 \times 10^{-6}$ (Baertschi, 1976) and $^{17}O/^{16}O = 382.7 \times 10^{-6}$ (Kaiser, 2008).

Nitrate isotopes ($\delta^{15}N$, $\delta^{18}O$ of NO_3^-) can help to identify the origin of NO_3^- contamination given each NO_3^- source shows an expected range of "δ" values (Fig. 2). For example, the $\delta^{15}N$-NO_3^- values typically exceed + 15 ‰ when originating solely from manure or sewage wastes, $\delta^{15}N$-NO_3^- values range from 0 ‰ to + 15 ‰, when originating from soil and are < 0 ‰ when originating solely from nitrified synthetic fertilizers or NH_4^+ in rain (Heaton, 1986; Mariotti et al., 1988; Fogg et al., 1998; Kendall, 1998; Bateman and Kelly, 2007). The $\delta^{18}O$-NO_3^- values are typically >+25 ‰ or <+20 ‰ when nitrate synthetic fertilizers are present or any other terrestrial source, respectively, and >+60 ‰, when nitrate originates from atmospheric deposition (Wassenaar, 1995; Kendall, 1998; Mayer et al., 2002). On a global scale the $\delta^{15}N$-NO_3^- values in river waters and groundwater typically vary between ~ -10.0 ‰ and + 30 ‰ due to multiple nitrate pollution sources and N-cycling processes (Matiatos et al., 2021). On the other hand, the $\delta^{15}N$-NO_3^- values in precipitation typically range between ~ -15.0 ‰ and ~+15.0 ‰ due to the influence of a variety of factors, including the sources of nitrogen (e.g., power generators, vehicles, agriculture), the mechanisms by which it is transformed and transported in the atmosphere, and the conditions under which it is deposited on the surface (Song et al., 2021).

In addition to tracing the origin of nitrate contamination, nitrate isotopes also provide insights into the fate of nitrogen contaminants. Microbial processes, such as nitrification, denitrification, or volatilization can alter the concentration of nitrate and other nitrogen species, depending on the physical and chemical conditions. This can lead to changes in the isotopic fractionation of ^{15}N and ^{18}O of NO_3^- (Böttcher et al., 1990; Matiatos et al., 2021). The isotopic fractionation factor a, which is defined as the ratio of the reaction rate for two isotopes, is a key measure of these processes (Sebilo et al., 2006):

For nitrogen

$$a_N = \frac{k^{15}N}{k^{14}N} \quad (2)$$

For oxygen,

$$a_o = \frac{k^{18}O}{k^{16}O} \quad (3)$$

where a is the isotopic fractionation factor, and $k^{15}N$, $k^{14}N$, $k^{18}O$, $k^{16}O$ are the instantaneous reaction rates for the molecules containing ^{15}N, ^{14}N, ^{18}O and ^{16}O, respectively.

The isotopic enrichment factor, ε (for nitrogen ε_N and for oxygen ε_O), expressed in ‰ is defined as:

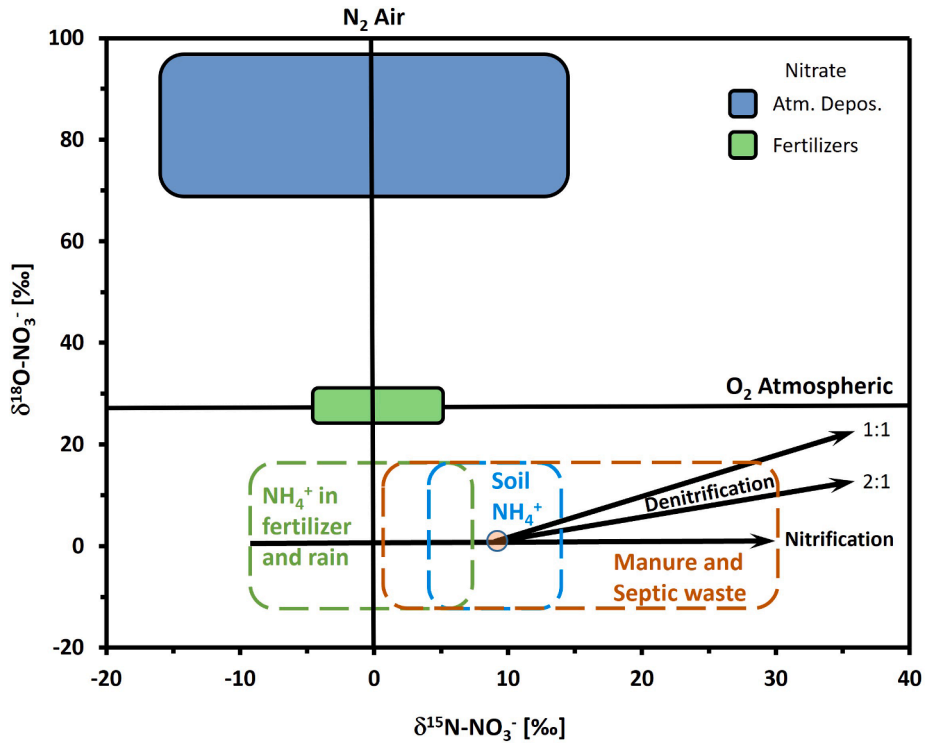

Fig. 2. Expected ranges of values of $\delta^{15}N$ and $\delta^{18}O$ of nitrate from various N sources. The arrows show indicative trajectories resulting from the denitrification of nitrate (modified from Kendall et al., 2007).

$$\varepsilon = 1000(a-1) \tag{4}$$

The following relationship between the rate of production of the isotopic forms of the product can be derived:

$$\frac{\left(\frac{d^{15}N_p}{dt}\right)}{\left(\frac{d^{14}N_p}{dt}\right)} = \left(10^{-3}\varepsilon + 1\right)\left(\frac{^{15}N_s}{^{14}N_s}\right) \tag{5}$$

(N_S nitrogen in the substrate and N_P nitrogen in the product) or

$$\frac{\left(\frac{d^{18}O_p}{dt}\right)}{\left(\frac{d^{16}O_p}{dt}\right)} = \left(10^{-3}\varepsilon + 1\right)\left(\frac{^{18}O_s}{^{16}O_s}\right) \tag{6}$$

Denitrification with the reduction of nitrate (NO_3^-) and nitrite (NO_2^-) to gaseous nitrogen (N_2) and nitrous oxide (N_2O) is a strongly fractionating process that results in a significant increase of the $\delta^{15}N$ and $\delta^{18}O$ values of the residual nitrate with a typical $\delta^{15}N$:$\delta^{18}O$ ratio of 1:2 (Kendall, 1998). Thus, denitrification is a reactive loss of NO_3^-, which generates higher nitrate isotope values than those of a simple dilution by hydrological dispersion processes, which are non-fractionating (Semaoune et al., 2012). Another fractionation process is assimilation, which refers to the transformation of oxidized N species, like NO_3^-, to NH_4^+ before being consumed by aquatic organisms. The isotope fractionation of the NO_3^- substrate due to assimilation typically yields a change to approximately 1:1 in the $\delta^{15}N$:$\delta^{18}O$ ratio of NO_3^- (Kendall et al., 2007), which is larger than that of the denitrification process. Lastly, nitrification is described by two partial oxidation reactions mediated by autotrophic organisms, which result in the production of intermediate species, such as nitrite (NO_2^-), and has nitrate (NO_3^-) as its final product. The influence of ^{18}O in water and molecular O_2 on the ^{18}O of NO_3^- produced during nitrification is typically described using a simple isotope mass balance equation (Kendall, 1998):

$$\delta^{18}O - NO_3^- = \frac{2}{3}\delta^{18}O - H_2O + \frac{1}{3}\delta^{18}O - O_2 \tag{7}$$

N transformation processes are associated with different degrees of isotopic fractionation. For example, incubation experiments showed that nitrate reduction during denitrification can range between −52.8 and −10.0 ‰ depending on the bacteria culture, the temperature, the moisture and the substrate availability (Denk et al., 2017; Rohe et al., 2014; Snider et al., 2009; Lewicka-Szczebak et al., 2014). The isotopic fractionation due to nitrification is variable depending on the oxidation stage. For example, the oxidation of NH_4^+ oxidation to the intermediate product of NO_2^- can induce an isotopic fractionation from −38 to −24 ‰ (Casciotti et al., 2003; Mariotti et al., 1981), whereas the oxidation of NO_2^- to NO_3^- triggers an enrichment of + 13 ‰ (Casciotti, 2009). Granger et al. (2010) showed that the isotope effect of assimilation can vary between + 0.4 to 8.6 ‰ depending on the plankton strains.

Due to the different impacts of the transformation processes on nitrate isotope ratios, isotopic fractionation may give insights into the relative importance of individual nitrogen cycling processes at the catchment scale when aided by water quality models, in particular by reactive solute transport models. The results of those models are strongly linked to water flow models, as the travel time distribution of water flows (transit times, see section 3) controls the reaction time at the water-substrate interfaces, with longer transit times favoring nitrate removal (Tanner and Kadlec, 2013; Yang et al., 2021).

Besides these relatively traditional tracers, $\Delta^{17}O$ (= $\delta^{17}O$ – 0.52 × $\delta^{18}O$, also referred to as the ^{17}O-excess) tracks the mass-independent fractionation through systems (Michalski et al., 2003) and can provide additional constraints on nitrate dynamics in watersheds. $\Delta^{17}O$ is particularly sensitive to the atmospheric deposition of nitrate and was used by Liu et al. (2013) to estimate a contribution of 0–7 % from atmospheric deposition to the nitrate in the Yellow River in China. More recently, Ji et al. (2022) used the tracers ^{17}O, ^{18}O and ^{15}N to study the relative contributions from atmospheric deposition, nitrogen fertilizer, soil nitrogen, and municipal sewage to a river network in eastern China.

Further, ^{17}O was used as a natural tracer for the gross nitrification rate of a temperate forest leaching nitrate into the stream (Huang et al., 2020). In addition, ^{17}O in water can be used to better quantify water flow, and measurements of ^{17}O in water have recently become more feasible due to developments in isotope measurement techniques (Kim et al., 2022; Terzer-Wassmuth et al., 2023; Xia et al., 2023).

So far, nitrate isotopes have been commonly used in statistical mixing models to calculate the proportional contributions of nitrate sources in water samples based on the assumption that any change in isotopic composition is the direct result of mixing of two or more sources of known composition (Xu et al., 2016). Source apportionment models, such as IsoSource (Phillips and Gregg, 2003), IsoError (Phillips and Gregg, 2001), and IsoConc (Phillips and Koch, 2002), have been applied in the past but do not consider possible changes in the isotopic composition due to fractionation-related processes. More recently, the MixSIAR model (Parnell et al., 2010) can better constraint the uncertainties (seasonal variation of isotopes, multiple sources > 3, and isotope fractionation). In brief, the MixSIAR model computes the proportional contributions of potential sources to the mixtures (samples) through their tracers (stable isotopes) after applying a Marchain Monte Carlo method to estimate the probability distribution (Stock et al., 2018). The overlap of isotope composition between different nitrate sources and the spatial variability in the isotope value of mixing water decrease the accuracy of these models. Some studies have successfully used these models to quantify nitrate sources in water environments (Xue et al., 2012; Matiatos, 2016; Re et al., 2021; Torres-Martínez et al., 2021; He et al., 2022; Yuan et al., 2023). More recent studies (e.g., Ji et al., 2022; Wu et al., 2023) have coupled these Bayesian mixing models with uncertainty analysis based on a probability statistical method introduced by Ji et al. (2017).

3. Catchment-scale water flow and quality models

Modeling the flow of water through a catchment and the transport of solutes is becoming an increasingly interdisciplinary field. New challenges arise from the need to keep the description of multiple interacting processes across different scales and parts of a catchment physically and numerically consistent. Due to this complexity, there are various models and concepts for simulating processes within a catchment, which are overall divided into physically-based models and conceptual models (Fig. 3).

Physically-based models are based on an understanding of the physical processes involved, and incorporate mass conservation principles (e.g., the Richards equation used in the ParFlow or HydroGeoSphere model (Brunner and Simmons, 2012; Maxwell et al., 2014) or the advection–dispersion equation as applied in the PHAST or MT3D-USGS models (Parkhurst et al., 2010; Bedekar et al., 2016). These models require robust numerical techniques to solve the equations and provide

		Water compartment	References
Conceptual models	•TRANSEP	SW	Weiler et al. (2003)
	•DYNAMIT	SW	Hrachowitz et al. (2013)
	•INCA	SW	Whitehead et al. (1998)
	•HBV	SW, S, GW	Bergström (1995), Lindström et al. (1997)
	•SAS FUNCTIONS	SW	Hrachowitz et al. (2021)
Physically-based models	•SWAT/SWAT+	SW, S	Arnold et al. (1998)
	•MODFLOW-MT3D-MS	GW, S	McDonald and Harbaugh (1988)
	•DAISY	S, UZ	Hansen et al. (1991), Abrahamsen and Hansen (2000)
	•SOIL-N	S, UZ	Johnsson et al. (1987)
	•ANIMO	S, UZ	Rijtema and Kroes (1991)
	•LEACHN	S, UZ	Wagenet and Hutson (1989)
	•WAVE	S, UZ	Vanclooster et al. (1995)
	•NLEAP	S, UZ	Shaffer et al. (1991)
	•Agriflux	S, UZ	Banton and Larocque (1997)
	•Coupmodel	S, UZ	Jansson and Karlberg (2004)
	•SWAP	UZ, SZ	Kroes and Van Dam (2003)
	•DRAINMOD	UZ, SZ	Skaggs (1978)
	•ANTHROPOG	UZ, SZ	Carluer and de Marsily (2004)
	•SHETRAN	SW, GW	Birkinshaw and Ewen (2000)
	•HydroGeoSphere	SW, GW	Therrien et al. (2006)
	•CWSS	SW	Reiche (1994)
	•MIKE-SHE	SW	Refsgaard et al. (1999)
	•NMS	S, UZ	Lunn et al. (1996)
	•INCA	SW	Whitehead et al. (1998)
	•CATFLOW	SW	Maurer (1997), Klaus and Zehe (2011)
	•HYDRUS	UZ, SZ	Šimunek et al. (2006)
	•AQUASIM	S, UZ	Reichert (1994)
	•CE-QUAL	SW	Buchak and Edinger (1982)
	•HSPF	SW, S	Bicknell et al. (1996)
AI models	•ANN	SW, GW	Maier and Dandy (1995), Gümrah et al. (2000)
	•Fuzzy-logic	SW, GW	Altunkaynak et al. (2005), Tutmez et al. (2006)
	•Kernel-based models	SW, GW	Wang et al. (2011), Hao et al. (2011)
	•Wavelet	SW, GW	Kang et al. (2007), Sreekanth et al. (2011)
	•Hybrid	SW, GW	Zhao et al. (2005), Tutmez et al. (2006)

Fig. 3. Examples of water quality models with applications for nutrients transport. SW: Surface water, S: Soil, GW: Groundwater, UZ: Unsaturated zone, SZ: Saturated zone.

high-resolution spatiotemporal outputs (Ashby and Falgout, 1996). Physically-based models are continually evolving, driven by advances in computational methods and power, laboratory and field experiments, and the need to better understand and predict impacts on water flow and solute transport due to, for example, changes in land use changes climatic conditions.

Conceptual models, unlike physically-based models, use transfer functions that are not necessarily based on physical knowledge but describe flow and transport in a physical meaningful (conceptual) way to convert a measured input signal to an output signal. For example, the TRANSEP model uses gamma and beta distributions as transfer functions to transform precipitation into runoff (Schmieder et al., 2019), whereas the DYNAMIT model uses process-based StorAge Selection (SAS)-functions to link the age distribution of water stored in a catchment to the age distribution of water in runoff (Hrachowitz et al., 2013, 2021). Conceptual models can also be further classified into subclasses such as "lumped", "black-box" or "white-box", and "semi-mechanistic" models (Braake et al., 1999). However, in practice, model types often overlap. For example, physically-based models use simplifications due to the limited spatiotemporal resolution of soil and geological structures and hydrometeorological measurements needed to calibrate them, while knowledge of physical processes is incorporated into conceptual models. For a detailed overview of recent model developments using time-variable water flow we refer to Benettin et al. (2022).

Models at the catchment scale often consist of a combination of individual models for the simulation of environmental subareas such as the root zone, groundwater, and surface water (Fu et al., 2019). The couplings between these single environmental subarea models can range from sequential to fully coupled with complete feedback mechanisms between the different environmental domains. Integrated catchment models may consist of a single model approach or a combination for the whole catchment. An example of a stand-alone integrated conceptual model is the Soil and Water Assessment Tool (SWAT) model. Examples of a combined approach are STONE (Wolf et al., 2003), with a chain of many model codes; the Hydrologiska Byrans Vattenbalansavdelning (HBV)-N (Arheimer and Wittgren, 2002) model, where the physically-based root zone model SOIL-N is used together with a lumped conceptual catchment model HBV (Bergstrom, 1995; Lindström et al., 1997); a compound approach of Styczen and Storm (1993a,b) where the physical based root zone model (DAISY) was coupled with the distributed physically-based catchment model (MIKE SHE); and an integrated approach is the SWATMOD model (Sophocleous et al., 1999; Bailey et al., 2017), which uses the root zone part of SWAT together with the physically-based groundwater model MODFLOW. In the study of Conan et al. (2003) this latter model was used together with MT3DMS (Zheng and Wang, 1999) for nitrate transport modeling.

As a relatively new alternative to the aforementioned model-types, machine learning (ML) models (as part of Artificial Intelligence) are emerging in environmental sciences (Beven, 2020; Gonzales-Inca et al., 2022; Mosaffa et al., 2022) (Fig. 3). ML methods are being applied to large data sets to improve scientific understanding and increase the efficiency of data processing and management, though their full potential has not yet been completely exploited (Beven, 2020). For example, Bhattarai et al. (2021) evaluated nine different ML algorithms for simulating nitrate and phosphorus concentrations in five different watersheds. Their analysis revealed that land use and related nitrate inputs (diffuse vs point sources) were determinant in the quality of results, having obvious implications for the prediction of nitrate fate. Artificial Neural Networks (ANN) performed best for rivers/streams in urban and agricultural watersheds, while Regression Trees with Bayesian Optimization (RT-BO) performed best for the forested watershed. Similarly, Wang et al. (2021b) applied ML methods to simulate nitrate concentrations and other contaminants in streams for the Texas Gulf Region, assessing the effect of urbanization in the region. These above-mentioned model types profit from advancements in satellite data availability, sensor technology and rapid transfer of data, improved computational power and increasing availability of data from "uncommon" measurements such as nitrate isotopes.

3.1. Conceptual models

Conceptual models use transfer functions that do not necessarily have a physical process basis to turn an input signal into an output response. The transfer functions may simulate the variable(s) of interest even if the function itself is not based on any physical process. The catchment is often represented as a black box, meaning that the spatial process distribution in the catchment is not represented. These models usually do not have spatial variation in model parameters or results, so they "lump together" the spatial and sometimes temporal heterogeneity of a catchment (lumped models). However, these "lumps" can be smaller than the total catchment area when using the concept of hydrological response units (HRU), which are areas of a catchment that produce the same output response to an input signal. These semi-distributed models allow for some variability but have less spatiotemporal resolution than a fully distributed physically-based model.

One example of a simple water flow model is the fraction of young water approach (Kirchner, 2016). This approach uses the ratio of sine wave amplitudes fitted to $\delta^{18}O$ or $\delta^{2}H$ tracer input and output signals to estimate the percentage of river water that is younger than approximately three months. The only input variables are the input and output tracer signals, as well as precipitation and streamflow measurements for weighing the tracer signals. The advantage of this approach is its ease of use, even in data scarce catchments. However, the temporal resolution of the tracer data has been shown to influence the obtained results (Stockinger et al., 2016). It can be used to derive temporally varying results (Stockinger et al., 2019) or runoff-dependent results (von Freyberg et al., 2018). The main disadvantage is that it does not provide any insight into process knowledge for the obtained results and it does not include equations or storage components representing catchment flows and storages, so it cannot be used for detailed solute transport. The only way it can be linked to solute transport is by the general conclusion that on average a certain percentage of river water is younger than three months, which allows for a rough estimate of solutes quickly passing through the catchment. However, this approach does not consider reaction dynamics in the soil, making it unsuitable for coupling with (reactive) solute transport, especially for nitrate transport. Nitrate is not a conservative tracer and reacts during nitrification and denitrification processes. Thus, even if the input and output of nitrate were perfectly well defined, incomplete knowledge about the biogeochemical transformations nitrate is exposed to would lead to errors in estimating nitrate transport through a catchment. Since the fraction of young water approach features no conceptual boxes that represent the unsaturated zone or the groundwater zone, it cannot be directly improved by equations describing nitrification and denitrification in those catchment domains. The sole result of the fraction of young water is a percentage estimate of water younger than three months in streamflow, and any modifications of the nitrate input signal must be computed separately.

Another simple approach is the use of a convolution integral. The convolution integral approach is a mathematical method that is similar to cross-correlation of two time series, with one of the time series being reversed. It is commonly used in hydrology, particularly in the analysis of precipitation time series. The approach involves convolving the precipitation time series with a transfer function that can take on various mathematical shapes, such as a beta or gamma distribution. The transfer function represents the proportion of a past rainfall event that arrives at a certain point in time, effectively modeling the transit time distribution (TTD) of a catchment (Botter et al., 2013). The convolution integral approach is included in many conceptual box models, such as the TRANSEP model (Weiler et al., 2003), and is relatively easy to implement, however, subjective choice has to be made about the shape of the transfer function. Previous studies have used the approach as a time-invariant TTD (Stockinger et al., 2014), even though transit times can

vary over time (Basso et al., 2015). SAS functions (Harman, 2015; Rinaldo et al., 2015) have been proposed as an alternative to capture time-variance in transit times more effectively (see next paragraph for more details). The ability to couple the TTDs derived from the convolution integral approach to nitrate transport depends on the model structure used. Simplistic model structures make it difficult to incorporate solute transport, as they cannot account for spatial heterogeneity in nitrate reaction dynamics, both horizontally from a point in space to another that might have different land use or nitrate inputs, and vertically, through different soil depths where the soil water content and thus nitrification and denitrification conditions might strongly differ. An alternative approach would be to incorporate reaction equations into the water flow model itself, modifying the nitrate concentrations based on biogeochemical processes occurring in the conceptual box, prior to transportation of the nitrate input signal by the water with transit times defined by the TTD. Yang et al. (2021) already used nitrate as an additional tracer to constrain estimates for water flow and incorporated simple nitrate reaction dynamics.

SAS functions connect the age distribution of water (i.e., water ages are often defined as specific metrics, such as travel time, residence time or young water fractions to provide insights into mechanisms of variations in flow paths, Kirchner et al., 2000; Botter, 2012; McDonnell and Beven, 2014) stored in catchments to the age distribution of the river water at any given point in time. Thus, these functions show when and under which conditions a catchment mainly releases water of a specific age (e.g., dominantly releasing young water from soil storage to become streamflow). For example, Hrachowitz et al. (2021) used SAS functions to demonstrate that after deforestation, the catchment released a larger proportion of young water compared to before deforestation. Understanding the concept of different water ages within catchments is important because water transports nitrate, and nitrate concentrations can vary with water age. For example, old fractions of groundwater can be more enriched in nitrates due to legacy effects from long-term fertilizer application or depleted in nitrate due to denitrification (Wang et al., 2013; Erostate et al., 2018; Lutz et al., 2022; Matiatos et al., 2022). With the time-variant nature of SAS functions, it is theoretically possible to incorporate time-varying nitrate dynamics, making SAS functions even more suitable for adding nitrate information to water flow models compared to convolution integral approaches.

So far only water stable isotopes and no nitrate isotopes have been used in conceptual models to elucidate hydrological processes, such as the fractions of water composing the runoff. For example, Weiler et al. (2003) coupled a TRANSEP model with water stable isotopes to separate the storm hydrograph. In another study, Segura et al. (2012) modelled catchment rainfall-runoff and stable isotope tracer response using a lumped conceptual model that integrates the unit hydrograph and isotope hydrograph separation methodologies. A more detailed review of the use of water stable isotopes in hydrograph separation can be found in Klaus and McDonnell (2013). On the other hand, Benettin et al. (2017) applied a transport model through the "direct-SAS" approach to reproduce the observed δ^2H values and unravel travel time distributions in a river catchment. In the same work, the authors highlight the challenge of using SAS functions in the application to large-scale transport of harmful chemicals like nitrates, and in the proper estimation of solute mass loads exiting a catchment.

3.2. Physically-based models

In physically-based hydrological models water flow and solute transport in both the surface and subsurface domain, including soils, are typically governed by the Richard equation and advection–dispersion equations, which consider flow and sorption/desorption of contaminant, but also contaminant exchange between surface and subsurface due to infiltration, diffusion and bed exchange (Frey et al., 2021; Schilling et al., 2022; Peel et al., 2023).

Physically-based models can cover only a single environmental subarea, such as the root zone, or the entire catchment using spatially distributed catchment models, seeking to describe the water and nitrate processes using numerical solutions for partial differential equations. To name a few examples of root zone models are DAISY (Hansen et al., 1991; Abrahamsen and Hansen, 2000), SOIL-N (Johnsson et al., 1987), and ANIMO (Rijtema and Kroes, 1991). Examples of river and lake oriented models are AQAUSIM (Reichert, 1994) and CE-QUAL (Buchak et al., 1982). Due to the complex behaviour of nitrogen in soils, several models have been specifically developed for modeling nitrogen transformations and nitrate leaching. Examples are LEACHN as part of the LEACHM model (Wagenet and Hutson, 1989), WAVE (Vanclooster et al., 1995), NLEAP (Shaffer et al., 1991), Agriflux (Banton and Larocque, 1997), and Coupmodel (Jansson and Karlberg, 2004). An intercomparison of these models can be found in Diekkrüger et al. (1995) and Smith et al. (1997). One-dimensional models, such as SWAP (Kroes and Van Dam, 2003) or DRAINMOD (Skaggs, 1978; Moursi et al., 2022) have been widely used for simulating flow and solute transport through the saturated and unsaturated zones, whereas an example of 2D models to simulate unsaturated and saturated water flow is ANTHROPOG (Carluer and de Marsily, 2004).

To upscale results, catchment scale models are typically used. The physically-based, semi-distributed and process-oriented SWAT model (Arnold et al., 1998; Abbaspour et al., 2015; Nguyen et al., 2022) used the representative elementary watershed concept by dividing the simulation domain in hydrologic response units to simulate water flow, solute transport, and sediment transport in agricultural catchments. Nitrogen transformations can be simulated with SHETRAN, a physically-based, spatially distributed river catchment model, that can be used in three-dimensions for coupled flow and nitrate transport (Birkinshaw and Ewen, 2000). For example, in SHETRAN, the subsurface is a variably saturated heterogeneous region, comprising perched, unconfined and confined aquifers, and unsaturated zones, and at the surface there is vegetation, overland flow and stream networks. The advection–dispersion equations are used for nitrate transport simulations with terms added for adsorption. The nitrogen transformations taking place are modelled using NITS (Nitrate Integrated Transformation component for SHETRAN). NITS has pools for both carbon and nitrogen in manure, litter and humus, further pools for ammonium and nitrate, and involves the simultaneous solution of seven ordinary differential equations plus several auxiliary equations.

A coupling between more mechanistic models for nitrogen transformation with more complex models for subsequent flow and transport models is quite common. For example, Bonton et al. (2012) combined the Agriflux (Banton and Larocque, 1997) and HydroGeoSphere (Brunner and Simmons, 2012) models to simulate transformation and transport of nitrogen compounds under variably-saturated flow conditions. The simulation for different agricultural parcels used the Agriflux model (Banton and Larocque, 1997) to simulate one-dimensional vertical flow and nitrate transport in the unsaturated zone and nitrogen transformation, where subsequently the HydroGeoSphere model is used to simulate transient groundwater flow and subsurface nitrate transport below the root zone. Zang et al. (2022) applied a quasi-3D feedback integrated model, accomplished by Hydrus 1D, MODFLOW, and MT3DMS. Overall, a small number of models have the capability for studying nitrate pollution in river catchments, including: CWSS (Reiche, 1994), DAISY/MIKE-SHE (Styczen and Storm, 1993a,b; Refsgaard et al., 1999; Seidenfaden et al., 2022), NMS (Lunn et al., 1996) and INCA (Whitehead et al., 1998). However, considerable advances have been made in physically-based spatially distributed river catchment modeling in the past few years, especially in relation to subsurface modeling, resulting in the development of SHETRAN (Ewen et al., 2000).

Further examples for comprehensive three-dimensional models are the physically-based catchment models HMSMOD (Panday and Huyakorn, 2004), MIKE SHE (Refsgaard and Storm, 1996), CATFLOW (Maurer, 1997; Klaus and Zehe, 2011), HydroGeoSphere (Therrien et al., 2006; Brunner and Simmons, 2012), Parflow (Maxwell et al., 2014), and

to some extent the finite-difference groundwater model MODFLOW (McDonald and Harbaugh, 1988; Harbaugh and McDonald, 1996) where surface water simulations typically have been based on simpler conceptual approaches. Moreover, the HYDRUS model can be applied in one to three dimensional simulations (Šimůnek et al., 2006, 2016). The coupled surface and subsurface HydroGeoSphere model (Brunner and Simmons, 2012) was used for example by Rozemeijer et al. (2010) to simulate the impact of drains in a 3D model to test an experimental tile drainage network in a Dutch agricultural sub-catchment, where nitrate transport occurred. Yang et al. (2022) investigated the dynamics of catchment-scale solute export from diffuse nitrogen sources. They highlighted that previous data driven studies suggested that the catchment topographic slope has strong impacts on the age composition of streamflow and consequently on in-stream solute concentrations. Yang et al. (2022) used the fully coupled surface and subsurface numerical HydroGeoSphere (HGS) to model groundwater, overland flow, and nitrate transport.

Another example is the SWAT model (Abbaspour et al., 2015). The physical processes associated with water and sediment movement, crop growth, and nutrient cycling are modelled at the HRU scale; runoff and pollutants exported from the different HRUs are routed downstream. SWAT simulates N cycling, which is influenced by specified management practices, such as planting, harvesting, tillage passes, and nutrient applications, among others. N is divided in the soil into two parts, each associated with organic and inorganic N transport and transformations, where N is added to the soil by fertilizers, manure or residue application, fixation by legumes, and rain. In the SWAT model nitrification is calculated as a function of soil temperature and soil water content, while volatilization as a function of soil temperature, depth, and cation exchange capacity. Plant uptake of N is calculated as the difference between the actual concentration of the elements in the plant and the optimal concentration, following a supply and demand approach. Denitrification that takes place in the nitrate pool is a flux of N to the atmosphere and is calculated as a function of soil water content, temperature, organic carbon content, and available mineral N. Overall, N cycle and N species transformations and transport in catchment models, such as SWAT, are governed by the hydrological cycle and are modelled based on simulation routines of natural processes and agricultural management that incorporate predefined parameters and coefficients.

Unlike nitrate isotopes, water stable isotopes have been extensively used in physically-based models. For example, Jafari et al. (2021) simulated surface-ground water interactions using a SWAT-MODFLOW model by integrating insights from water isotopes. The use of isotope allowed determining the relative contribution from different sources of water into aquifer recharge and identifying areas with high surface-ground water interactions. Manna et al. (2019) validated the results of a spatially distributed numerical model (MIKE SHE), which was used to simulate the responses to precipitation in a catchment, by comparing the water stable isotopes in groundwater with those of precipitation. In a more recent study, Zhou et al. (2021) used the HYDRUS-1D model to simulate variably-saturated water flow and solute transport in porous media, by including an option to simulate water stable isotope fate and transport while accounting for evaporation fractionation.

3.3. Artificial intelligence models

Artificial intelligence (AI) and ML are used to generate models from databases or to develop logic-based training algorithms. AI can sort and interpret massive amounts of hydrological and water quality data from various sources to carry out a wide range of tasks in data analysis to guide water management. The extracted information form databases using AI tools can help water related processes, validate conceptual and numerical hydrological and water quality models and develop non-parametric prediction tools (Singh and Gupta, 2012; Aldhyani et al., 2020). With regard to water quality models, a recent survey on the use of AI models showed that N-species are among the most preferred chemical variables to be simulated in river water quality (Tiyasha et al., 2021). Among the AI model types, the artificial neural networks (ANN), the fuzzy logic, the kernel based, the wavelet and the hybrid models are the ones that, till present, have been mostly used in the assessment of water quality in rivers using different types of architectures.

The ANN models typically use three or more layers (input, hidden and output) and the training is done using learning algorithms, such as backpropagation, generalized regression and Bayesian regularization (McCulloch and Pitts, 1943; Maier and Dandy, 1999; Gümrah et al., 2000; Antanasijević et al., 2014). There are several types of ANNs (e.g., feedforward networks, recurrent networks, convolutional networks), with feedforward networks being the simplest type, which consists of a series of layers of neurons, with each layer connected to the next, from the input layer to the output layer. For example, Stamenković et al. (2020) used a three-layer ANN model to predict the concentration of nitrates in the Danube River based on other water quality data.

On the other hand, fuzzy logic-based models are powerful tools for dealing with uncertainty and imprecision in systems that are complex or difficult to model using traditional mathematical methods (Jang, 1993; Altunkaynak et al., 2005; Tutmez et al., 2006). Fuzzy logic-based models rely on fuzzy sets, which are defined by a membership function that assigns a degree of membership to an element of a set. These models allow for the incorporation of human expertise and intuition into the modeling process, which can improve the accuracy of the model. For example, Scannapieco et al. (2012) used fuzzy-logic based models to assess the water quality in rivers relation to achieving good ecological status as mandated by the 2000/60/EC, or Water Framework Directive (WFD).

Kernel-based models are a powerful AI tool particularly when working with complex, nonlinear data sets used for pattern recognition, regression analysis, and other tasks. They are based on the concept of kernel functions, which transform input data into a higher-dimensional feature space, where it may be easier to identify patterns and relationships (Hao et al., 2011; Wang et al., 2011). They work by finding a decision boundary that separates the data into different classes or regions and they are generally more robust to noise and outliers and less prone to overfitting (Vapnik, 1998). For example, Kamyab-Talesh et al. (2019) used kernel-based models to predict the water quality index in rivers and identified nitrate as the most influential parameter on the index. In another example, Sajedi-Hosseini et al. (2018) used Kernel-based and other AI models to predict nitrate contamination in groundwater in Iran.

Other AI-related methods are wavelet algorithm models (e.g., Kang and Lin, 2007; Sreekanth and Datta, 2011; Yaseen et al., 2018), which are able to decompose a signal at specific scales and positions, which allows for the extraction of information from different frequency bands, and hybrid models, which are a combination of two or more different AI techniques capable of solving complex problems (e.g., Zhao et al., 2005; Tutmez et al., 2006; Nourani et al., 2014). These models aim to leverage the strengths of different AI techniques and overcome their limitations to create more efficient and accurate solutions. AI is also able to recognize patterns and analyse high resolution images on land use (e.g., deforestation) and water status (e.g., eutrophication) from satellites and drones to detect regional and global changes (e.g., Das et al., 2022). Often AI and ML are used in hybrid models that combined physics-based and data-driven models (IAEA, 2022). This is also done at a more fundamental level to model the small-scale turbulent structures that can be present in fluid flows (Stoffer et al., 2021) and ultimately affect the main flow and dispersion of the suspended or dissolved substances, including nitrate in hydrological catchments.

Efforts to use AI techniques in isotope-related studies are still scarce and focus mostly on water stable isotopes. For example, Nelson et al. (2021) used an AI model to predict water stable isotope time series in precipitation in Europe with the aim to address the lack of sufficient measurements spatially and in the long-term, which limits the use of the available values to assess hydrological and meteorological processes.

Cemek et al. (2022) used different AI techniques to predict the isotopic composition ($\delta^{18}O$ and $\delta^{2}H$) in groundwater, whereas, more recently, Erdélyi et al. (2023) combined conventional regression techniques with Random Forest to predict the water stable isotope composition of precipitation in areas with large spatial data variability. Sahraei et al. (2021) used AI techniques and physical and hydrological variables (e.g., meteorological data, catchment wetness, water temperature, pH) to predict water stable isotopes in streams and groundwater. In relation to nitrate isotopes, Yang et al. (2021) developed an AI model to predict the $\delta^{15}N\text{-}NO_3^-$ values in surface waters by using conventional hydrochemical variables, that could enhance the interpretation of $\delta^{15}N\text{-}NO_3^-$ data and potentially improve water quality management. However, at present the accuracy of ML based prediction is often insufficient to allow for autonomous decisions and is subject to data accessibility.

In the adjacent field of air quality and atmospheric pollution, machine learning methods were used inside an 'emulator' that mimics the behaviour of computationally demanding models, to find sources of pollution (Fillola et al., 2022). Many of the machine learning methods used for such models are not domain-specific and development of similar models for pollution in hydrological catchments could benefit from these existing models from other domains. Single application or in combination with other tools, ML provides new insight into the relationship of variables that enable to account for highly non-linear and non-homogenous models and in non-stationary and dynamic environments. For example, Vystavna et al. (2021) showed that relative humidity, air temperature and variables related to energy processes (e.g., solar radiation), control the water stable isotopic composition in lakes and consequently their evaporation rates.

4. Model limitations and uncertainties

Each model type has its advantages and limitations, and the challenges posed to the model user that wants to represent both water flow and solute transport through a catchment are multifaceted (Fig. 4). Many modeling studies rely on simple empirical models when simulating nitrate pollution at the catchment scale because these model concepts can reflect their judgments and uncertainties (Quinn, 2004). Another approach is to apply physically-based, distributed models within complex, three-dimensional heterogeneous landscapes, potentially inducing equifinality (Beven, 2006 and reference therein) and predictive uncertainty problems. In physically-based models, a large amount of model parameters must be either provided from measurements or calibrated to characterize processes in all components of the water balance. For example, model parameters related to the interaction between surface, soil and ground waters, or those related to transport mechanisms and reaction rates of solutes must be provided, but existing measurements are often only available as sparse field or literature information.

Furthermore, the challenges in developing reliable and efficient models are associated with spatiotemporal heterogeneity in parameters and state variables, data quality uncertainties, nonlinearities, and scale effects in process dynamics, as well as complex initial system states and boundary conditions, which might be poorly understood (e.g., Gauthier et al., 2009). Although these models are physically-based and can simulate complex environmental processes, model parameters cannot be uniquely determined due to the uncertainty in state variables (e.g., observed discharge rates, groundwater levels) or because these state variables have not enough information content to uniquely calibrate model parameters. This can lead to large predictive uncertainty or numerical overfitting and errors, strongly impacting water management decisions (Sordo-Ward et al., 2016).

In contrast, a conceptual model approach relies on the simplification of a model structure, which on one hand limits the capability of the model to inform about catchment internal processes, but on the other hand it allows for a much more robust parameter optimization using millions of model-runs in inverse modeling with a limited number of available measurements of hydrometeorological variables. Thus, conceptual models are easily calibrated, with the caveat that multiple equally feasible parameter sets can be found (equifinality). Some studies (e.g., Orth et al., 2015; Moeck et al., 2016) have shown that a simple model could simulate discharge and other variables equally well and, in some cases even better. However, if an event (e.g., an extreme runoff event, or unseen drought) has not been observed in the historical calibration dataset, it cannot likely be simulated as the model lacks

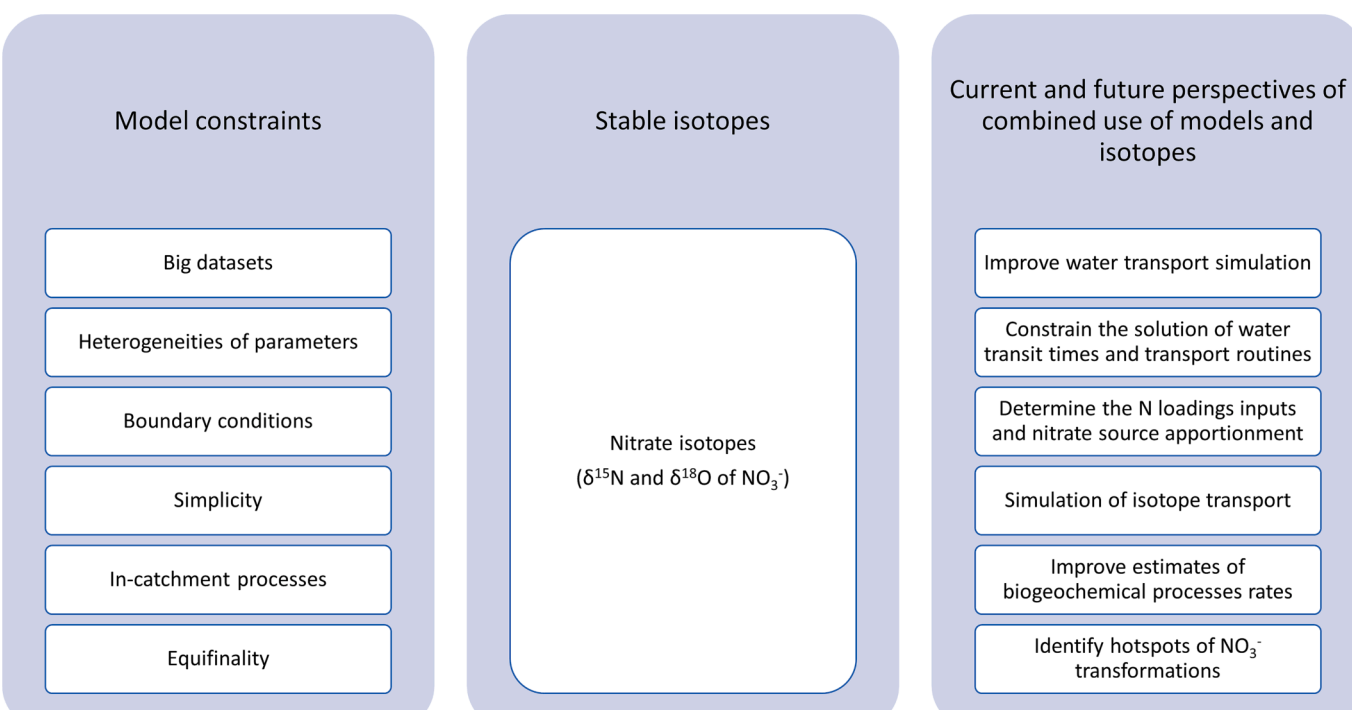

Fig. 4. Model limitations and perspectives of combining stable isotopes with modeling techniques.

information about the processes leading to this event.

ML tools can sort and process massive amounts of data from various sources, generate models from datasets or logic-based algorithms and carry out a wide range of tasks with high predictive accuracy (Xu and Liang, 2021). However, they are still not easily interpretable. Although high predictive accuracy is crucial to all modeling tasks, it is often not the only purpose. Especially when dealing with complex systems, as is the case in catchment modeling, learning about the system behavior and understanding its internal and external interrelationships are essential. However, research on explainable AI or "interpretable machine learning" (e.g., Montavon et al., 2018; Samek et al., 2019; Molnar et al., 2020) has strongly advanced in recent years, and catchment modeling and ties between internal model states and hydrological processes are being elucidated (Lees et al., 2021). A promising ML algorithm, SHapley Additive exPlanations (SHAP), which measures the impact of variables considering the interaction with other variables, has been applied recently as an interpretable machine learning approach. SHAP algorithm calculates the importance of a feature by comparing what a model predicts with and without the feature (Aydin and Iban, 2022).

No matter which model and approach is used, another often-ignored limitation is the time lag, which is difficult to simulate. As mentioned earlier this time lag of water and solute transport through the unsaturated and saturated zone paired with biochemical lag time must be quantified to obtain realistic and sound model predictions (van Meter et al., 2016). The specific time lag is, however, very scale and location dependent and can differ according to climate, pedology, landscape and land use management (Vero et al., 2018). The spatial and temporal heterogeneity of the physical properties of the watershed, the extent of chemical processes and transformations, the length of residence times throughout the subsurface, and the influence of climatic and meteorological conditions that affect the overall time lag pose further challenges in producing sound simulations (Baillieux et al., 2015; Hocking and Kelly, 2016; Hrachowitz et al., 2016; Osenbrück et al., 2006; Van Meter et al., 2016; Vero et al., 2014, 2018). This is especially true for models that simulate only one or two compartments of the catchment and oversimplify other processes. Developing an approach that incorporates unsaturated, saturated, and surface components, biochemical factors, and appropriate scales would likely be helpful, but may be too data-intensive (Hrachowitz et al., 2016) This can lead again to model simplification or not enough data are available to determine model parameters in a trustworthy way.

In general, models capable of carrying out all tasks required to simulate and predict water quantity and quality, properly representing water flow and solute transport at the same time, are difficult to find in literature. Generally, the aim of many water flow models is to accurately predict runoff, which can be quite easily achieved with simple models. However, often several model setups and parameter sets can lead to similarly well-simulated runoff curves (the equifinality concept), making predictions outside of the calibration period difficult. Another issue with too simple models is their inability to aid in understanding catchment-internal processes if they do not contain elements in their structure that represent those processes.

5. The way forward and conclusions

Similar to coupling of water flow models with water stable isotopes to constrain their solution of water transit times, we propose coupling of solute transport models with nitrate isotopes to constrain the transport routines. For example, Yang et al. (2021) combined a simplified water quality model, in particular a nitrate reaction model of the soil zone, with a time-variable water flow routine and used, among other data, the measured nitrate concentrations in stream flow to calibrate the water flow routine. Since they used a nitrate reaction model, we argue that additionally using nitrate isotope data informing about nitrate reactions can additionally constrain the model, potentially leading to an even further improved estimate of water flow and transport. Changes in nitrate levels in various domains, such as the unsaturated zone, groundwater, and riverbed, could result in similar nitrate concentrations in runoff. However, to the best of our knowledge, nitrate isotopes have yet to be utilized in water quality models for simulating solute transport. This points to the necessity to further explore their applicability.

N loading input: Nitrate isotopes have the potential to enhance our understanding of not only the source, but also the fate of the initial nitrate or other N-species concentrations. They can help in determining the N loading input in a catchment and in understanding the dynamics of biogeochemical processes. For example, transport models like SWAT, often require users to select from a myriad of parameter combinations, making it challenging to ascertain which set of parameters accurately reflects a catchment's characteristics (Panagopoulos et al., 2011). Here, nitrate isotopes have a certain limit in the application but their role can be explored for the nitrate source tracing. Employing nitrate isotopes could greatly enhance our understanding of the total N output, when aggregating loads from different land use types and point sources. Using isotopic data to estimate the proportional contribution of nitrate sources assist modellers in conducting a more precise parameterization across the catchment, considering land cover types and topographical zones. This will help in the appropriate initialization and definition of N related parameters and coefficients. The problem of equifinality, the possibility of multiple plausible solutions, can thus be effectively mitigated by narrowing the solution space of spatially varying parameter combinations. This, in turn, would lead to more accurate model estimates of N loading at specific river locations, where observational data are available. For example, Husic et al. (2020) introduced nitrate isotope data in a statistical mixing model (MixSIAR) and coupled it with a transport model to apportion nitrate loading sources (soil, fertilizer, and manure) across three pathways (quick, intermediate, and slow) in a karst watershed. They found that approximately 60 % of nitrate is exported from the catchment, facilitated by the quick-fertilizer (16 %), the intermediate-manure (15 %), and slow-soil (27 %) pathways.

Biogeochemical processes: Additionally, nitrate isotopes can provide estimates of biogeochemical processes rates, such as of denitrification, thereby allowing for more precise calibration of the parameters used to simulate these processes. This can lead to more accurate model predictions of the actual N availability in soil that can be used by plants or can migrate to surface and groundwater. Models simulating the nitrogen cycle, like HSPF (Bicknell et al., 1996), can be suitable to use nitrate isotopes in order to validate and quantify the biogeochemical processes. On the contrary, models, which assume an unlimited nitrogen pool and thus biogeochemical transformation are overlooked, like INCA, seem more appropriate to benefit from the use of nitrate isotopes as tracers of origin.

Nitrate isotopes can also help to locate the hot spots of biogeochemical processes within catchments. The occurrence of biogeochemical processes may vary spatially and temporally. This implies that nitrate concentrations may be influenced not only by different nitrate pollution sources but also by varying N-cycling histories. Deutsch et al. (2009), for example, demonstrated that N-transformation processes (denitrification and assimilation) occurred along the Elbe River, which led to changes in nitrate concentration, thus showing in-stream N-transformations. Li et al. (2019a) found that around 12 % of nitrate was removed by denitrification in the Xijiang River during the dry season. N-transformation processes in the unsaturated and saturated zones may further complicate the modeling of nitrate concentrations, since rivers fed by groundwater may receive waters already subject to denitrification and with nitrate concentrations that do not truly reflect the origin of nitrate pollution. Riparian zones are also hot spots of NO_3^- transformation and removal, especially in agricultural catchments. A nitrate isotope survey in the Seine River Basin (France) found that riparian denitrification accounted for up to 50 % of NO_3^- removal in the Seine River and its tributaries during summer low-flow conditions (Sebilo et al., 2003; Sebilo et al., 2006). Moreover, wetlands, including marshes, bogs, and swamps, are biologically productive environments that

regulate NO_3^- removal primarily through plant uptake, microbial immobilization, and dissimilatory respiration processes. Reddy and DeLaune (2008) demonstrated that both denitrification and plant uptake of nitrate resulted in significantly lower NO_3^- concentrations in the outflow of a low-flow small temperate wetland compared to incoming stream water, resulting in an NO_3^- removal of 65–100 %.

Holistic understanding of the hydrological system: At present, the relatively high degree of uncertainty in water quality predictions limits their application in decision-making processes. To overcome this limitation, we propose that a primary objective should be to integrate catchment-scale water quality models with stable isotope approaches, specifically those focused on nitrate pollution. One of the key challenges lies in bridging the gap between the catchment hydrology (water flow) and water quality (solute transport) scientific communities. By integrating respective models, it becomes feasible to account for the complex interactions between water flow and solute transport, including the non-conservative behavior of nitrogen species. It is anticipated that a more complete representation of the underlying processes will foster a more holistic understanding of how hydrological systems work. For future model development and improvement, key trends involve the integration of different model types or the use of fully coupled, physically-based models. Overly simplified models or standalone models may not fully address the complexities of nitrate loadings and reaction dynamics. Therefore, models coupled with nitrate stable isotopes are necessary for obtaining the most plausible results. Incorporating observational data along with nitrate isotopes in the model will likely enhance the identifiability of model parameters and thus improve the predictability of water quality models. Ultimately, this will aid stakeholders in making informed decisions and addressing water-related issues more effectively.

Incorporation of AI models: AI models are progressively massively used in water quality studies but very scarcely in nitrate isotope surveys. However, their application so far is only tested theoretically and not in real conditions. Thus, the AI models developed should be tested against conventional and benchmarked models in catchment hydrology. AI models are also designed to perform specific tasks and may not perform well in new or unexpected situations due to lack of the ability to adapt to changing circumstances. Thus, the AI models should be trained on diverse datasets that cover a wide range of scenarios. The problem of missing or discontinuous data requires the use of additional AI models or can be overcome through the use of remote sensing applications. Additionally, recent technological advances in isotopic assays of nitrate (Altabet et al., 2019) have largely reduced the analytical cost to conduct high-frequency nitrate isotope analysis compared to the conventional techniques (Xue et al., 2010) and is expected to help overcome this drawback. Many AI models are black boxes, making it difficult to understand how they make decisions. Thus, more interpretable AI models that provide a clear understanding of how they make decisions or methods to extract explanations from the black-box models should be sought.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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